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Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" for organic chemists. Our main research interest is the elucidation of the resemblance and difference in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts is also studied.

Research Activities (Year 2003)

Presentations

Synthesis and Properties of the First Disulfur and Diselenium Complexes of Platinum, Tokitoh N, Nagata K, Takeda N, The 10th International Symposium on Inorganic Ring Systems, 17 - 23 August, Vermont, U.S.A.

Structure and Reactivity of Kinetically Stabilized Sila-aromatic Compounds, Shinohara A, Takeda N, Tokitoh N, 50th Symposium on Organometallic Chemistry, 28 - 30 September, Osaka, Japan.

Recent Progress in the Chemistry of Stable Sila-aromatic and Related Species, Tokitoh N, Kyushu International Symposium on Physical Organic Chemistry IX, 30 September - 3 October, Fukuoka, Japan.

Grants

Tokitoh N, Studies on the synthesis, structures, properties, and functions of novel aromatic compounds con-

taining heavier group 14 elements, Grant-in-Aid for Scientific Research (A)(2), 1 April 2002 - 31 March 2005.

Tokitoh N, Synthesis of dynamic complexes containing heteroatoms by taking advantage of kinetic stabilization, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2002 - 31 March 2006.

Tokitoh N, Synthesis of metallacyclopropabenzene derivatives by using bulky substituents and the elucidation of their properties, Grant-in-Aid for Exploratory Research, 1-April 2003 - 31 March 2004.

Kawai Y, Development of methods for the determination of the absolute configuration of chiral compounds using a novel crystalline agent, Grant-in-Aid for Scientific Research (C)(2), 1 Apr 2003 - 31 March 2005.

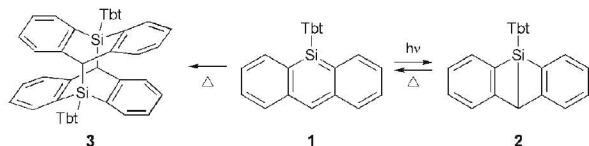
Takeda N, Synthesis of double bond species between group 10 metals and chalcogens and the elucidation of

Photochemical valence isomerization reaction of kinetically stabilized 9-silaanthracene

In recent decades, there has been much interests in the chemistry of $[4n+2]\pi$ -electron ring systems containing heavier group 14 elements, *heavy aromatics*, from the viewpoint of not only fundamental chemistry but also applied chemistry. Recently, we have succeeded in the synthesis and characterization of the first stable *heavy aromatics*, that is, silabenzene, 1- and 2-silanthralene, 9-silaanthracene, germabenzene, and 2-germanaphthalene utilizing an efficient steric protection group, Tbt group (*vide infra*). In addition, we have reported the photochemical isomerization of the silabenzene leading to the corresponding silabenzvalene derivative. Now, we investigated photochemical reaction of the 9-silaanthracene **1**.

When a C_6D_6 solution of **1** in a sealed tube was irradiated with light of $\lambda = 300$ – 500 nm through a UV cut filter at room temperature, the orange color of **1** disappeared and a new species, 9,10-Dewar-9-silaanthracene **2** was formed exclusively. **2** was found to undergo gradual thermal tautomerization into **1** even at -180 °C in hexane. Kinetic studies using UV/vis spectroscopy suggested that this reaction was a first-order reaction as well as thermal isomerization of 9,10-Dewar-anthracenes to anthracenes. In addition, the half-life time of **2** in hexane at 10 °C was estimated to be about 5 minutes. On the other hand, heating of a C_6D_6 solution of **1** at 110 °C in a sealed tube for 15 days or thermolysis of **1** in the solid state at 180 °C for 1 h afforded the corresponding [4+4]dimer **3**. **3** is thermally very stable and no cycloreversion to **1** was observed in the 1,2-dichlorobenzene- d_4 solution even at 200 °C.

These results are very interesting because it was experimentally demonstrated for the first time that 9-silaanthracene can afford either the Dewar-type isomer or [4+4] dimer depending on the reaction conditions.

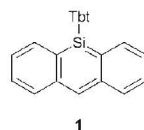


their properties, Grant-in-Aid for Young Scientists (B), 1 April 2003 - 31 March 2005.

Nagahora N, Syntheses, structure, and properties of novel low-coordinated species of heavier main group elements, Grant-in-Aid for JSPS Fellows, 1 April 2003 - March 2005.

Awards

Tokito N, The Chemical Society of Japan Award for Creative Work, Synthesis of Aromatic Species Containing a Heavier Group 14 Element by Taking Advantage of



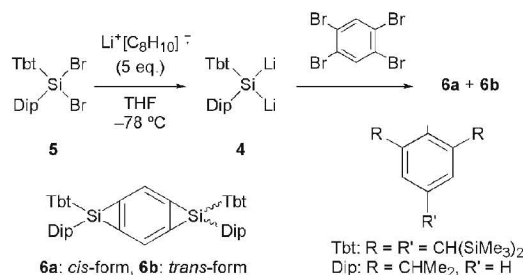
Left: solid state
Right: in C_6D_6



The first examples of stable benzenes fused with two three-membered rings: synthesis and structures of the two stereoisomers of bis(silacyclopropa)benzenes

Structures and properties of cyclopropabenzene derivatives have fascinated many organic chemists so far, because a competition between preservation of aromatic ring skeleton and angular strain in the three-membered ring fused to their aromatic ring results in unique properties. Recently, we have succeeded in the synthesis of the first stable diaryl sila- and germacyclopropabenzenes, heavier analogues of a cyclopropabenzene derivative, and reported their structures and physical properties. Now, we describe the synthesis of two stereoisomers of the first stable bis(silacyclopropa)benzenes, in which two silacyclopropene skeletons are fused to one benzene ring.

The reaction of dilithiosilane **4**, which was prepared by the exhaustive reduction of dibromosilane **5** using lithium naphthalenide, with 1,2,4,5-tetrabromobenzene at -78 °C in THF afforded the first stable bis(silacyclopropa)benzenes **6a** (cis-form) and **6b** (trans-form). The structures of **6a,b** were revealed by the X-ray crystallographic analysis. It was found that both of **6a,b** have no distinct bond alternation in their central benzene rings.



Kinetic Stabilization, The Chemical Society of Japan, 20 March 2003.

Tokito N, Humboldt Research Award, Systematic Studies on Homo- and Heteronuclear Doubly Bonded Compounds between Heavier Group 15 Elements, Alexander von Humboldt Foundation, 7 November 2003.

Takeda N, Progress Award in Silicon Chemistry, Japan, Stabilization of Low-coordinated Group 14 Element Compounds by Taking Advantage of Steric Protection, The Society of Silicon Chemistry, Japan, 18 October 2003.